

Chapter 3

Canadian Approach to the Environmental Characterization and Risk Assessment of Military Training

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The main goal of Canada's sustainable military training program is to maintain force generation and environmentally-friendly defense activities in order to ensure the long-term usage of military training areas. This paper will describe Canada's approach to the characterization of ranges and training areas, and also to perform appropriate risk assessments.

Literature Review

The Canadian sustainable military training R&D program, in agreement with the Sustainable Development Strategy promulgated by the Department of National Defence (DND) (1), is aimed at maintaining both military readiness and environmentally-friendly defence activities in order to ensure the long-term usage of military training areas. Moreover, as with many other countries, Canada has to deal with growing public concerns about environmental issues and is facing more stringent environmental laws. Indeed, the Fisheries Act (2) prohibits *any work or undertaking that could result in the harmful alteration, disruption or destruction of the fish habitat* by introducing deleterious substances in water, while the Canadian Environmental Protection Act (3) is concerned with pollution prevention and toxic substances releases. In addition, several compounds commonly found in military training areas are regulated by the

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Canadian Council of Ministers of the Environment (CCME) guidelines (4). Some of these compounds are also on the list of priority substances of the ARET program (Accelerated Reduction/Elimination of Toxics) that promulgates the voluntary reduction or near-elimination of the release of some of the most persistent, bioaccumulative and toxic substances in the environment (5). The U.S. Department of Defence (DoD), together with the Environmental Council of the States (ECOS) Sustainability Working Group and the Environmental Protection Agency (EPA), is also closely monitoring some emerging contaminants on military sites that could have a significant impact on DoD personnel and activities (6).

Within this context, Defence R&D Canada – Valcartier (DRDC Valcartier) initiated in the mid 90's a research program for the environmental assessment of the main ranges and training areas (RTAs) of the Canadian Forces (CF). Many studies, supported by Director Land Environment (DLE) Canada and Director General Environment (DGE) Canada have been conducted since then to better understand the nature and extent of contamination in RTAs (7–38).

In 2000, a six-year research project (ER-1155) was initiated by the U.S. Army Engineer Research and Development Center, Cold Regions Research Engineering Laboratory (CRREL, Hanover, U.S.) in collaboration with DRDC Valcartier under the Strategic Environmental Research and Development Programme (SERDP, Arlington, VA). The aim of this project was to study the deposition, accumulation, and fate of residues of energetic compounds at live-fire training ranges to determine the source terms for energetic contaminants. SERDP project ER-1155 was focussed on impact areas where cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX) was deposited and thus where the potential for groundwater contamination was the largest. A significant part of this work was performed in Canadian RTAs. SERDP project ER-1155 allowed the development of transport processes descriptors for the current explosives and their main transformation products (39–65). A protocol for the characterization of sites contaminated with energetic materials was written in 2003 under the umbrella of The Technical Cooperation Program (TTCP) (66). In 2009, EPA method SW-846 8330, used for the analysis of energetic materials, was updated to include sampling and processing methods (67), leading to EPA method 8330b (68).

Finally, SERDP project ER-1481 was initiated in 2006 to better understand the fate and transport of propellant residues at firing points (69, 70). Several studies have been performed on DoD and DND RTAs to better define the distribution and fate of propellant residues associated with live-fire training with munitions (71–91).

Background Information

Contaminants of Concern

Accurately detecting the type and quantity of contamination of munitions materials and their breakdown products in water, soil, sediment and biomass is vital to assessing the extent of contamination and ultimately the risk to human and ecological receptors. The contaminants of concern that might be dispersed

in the environment following live fire training are energetic materials, their decomposition products and metals.

Energetic Materials

Conventional weapons use energetic materials (EM) in the form of propellants, explosives, and pyrotechnics. A brief description of each type of EM is given below.

Explosives are classified as 'primary' or 'secondary' based on their susceptibility to initiation. Primary explosives, which include lead azide, lead styphnate, and mercury fulminate, are highly susceptible to ignition and are often referred to as initiating explosives, since they can be used to ignite secondary explosives.

Secondary explosives are much more prevalent on military sites than primary explosives. They include trinitrotoluene (TNT), 1,3,5-hexahydro-1,3,5-trinitrotriazine or research development explosive (RDX), octrahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine or high melting explosive (HMX), and 2,4,6-trinitro-phenylmethylnitramine or tetryl. Since they are formulated to detonate under specific circumstances, secondary explosives are often used as main charges or boosting explosives.

Secondary explosives fall into two main categories: (1) melt-cast explosives, based primarily on TNT, and (2) plastic-bonded explosives (PBX), which consist of a polymer matrix filled with a crystalline explosive such as RDX. Secondary explosives can also be classified according to their chemical structure. For example, TNT and trinitrobenzene are classified as nitroaromatics, whereas RDX and HMX are nitramines. The major classes of EM used by the military personnel throughout the world as well as their physical and chemical properties are reported in (66).

Propellants include both rocket and gun propellants. Most rocket propellants consist of a rubbery binder filled with an ammonium perchlorate (AP) oxidizer and sometimes powdered aluminum as fuel. Propellants may also be based on a nitrate ester, usually nitroglycerine (NG), nitrocellulose (NC), or a nitramine such as RDX or HMX. Gun propellants are usually single base (e.g., NC), double base (e.g., NC and NG), or triple base (e.g., NC, NG, and nitroguanidine (NQ)). Single-based propellants may also contain 2,4-dinitrotoluene (2,4-DNT) as an energetic plasticizer.

Pyrotechnic compositions are usually homogenized mixtures of small particles of fuels and oxidizers. High burning rates are obtained with particles of high surface area or high oxidizer content. Binders are sometimes used to turn the powder into a solid material. Typical fuels are based on metal or metalloid powders. Common fuels include metals (aluminum, magnesium, iron, zirconium, titanium, manganese, zinc, copper, tungsten, antimony, arsenic, etc), organic materials and polymers. Oxidizers are usually made of perchlorates, chlorates or nitrates. Several additives, both organic and inorganic, also act as opacifiers, colorants, flame suppressants, catalysts, stabilizers, anticaking agents, binders, plasticizers, curing or bonding agents.

Metals

The metallic composition of the shells and fusing system is generally proprietary information, and therefore little information is known about the proportion of heavy metal in a given munition. Most shells are made of steel, which is an alloy of iron and carbon, with several other metals added to modify their mechanical properties. Grenade shells are generally made of brass, an alloy of zinc and copper. Small arms bullets are made of a lead-antimony core contained in a brass jacket. However, other types of ammunition are made of several other metals, as shown by the large variety of metallic species detected in RTAs.

Issues and Sources of Munitions-Related Residues

Energetic Materials

It is now well known that normally functioning munitions (i.e. high order detonation) only spread about 0.001% of their explosive content in their surrounding environment (59–65). Therefore, most of the contamination in impact areas comes from UXOs that are cracked open by the detonation of an incoming round, by incomplete (low-order) detonations, by the destruction of duds using blow-in-place options, or by the corrosion of UXOs. In addition, UXOs pose a safety problem for troops, both in domestic training and in operations. A regular surface clearance of RTAs is often needed to get rid of surface UXOs. Additional UXO-related issues arise at the closure or decommissioning of RTAs, such as safety problems for the civilian population, huge costs of UXO detection and clearance operations, as well as government liability.

The most widespread compound of concern in impact areas is unexploded or deflagrated RDX, a common explosive found in Composition B and C4. RDX does not degrade in soil and, because of its solubility in water, has the potential to migrate easily to groundwater and outside the boundaries of military bases. This could trigger a serious environmental problem and even become a public health concern if the groundwater is used for crop irrigation or as drinking water.

Another ecological issue arises from the incomplete combustion of gun propellant in weapons and from the expedient burning of excess gun propellant bags on the soil at firing positions. Propellants contain significant amounts of carcinogenic and toxic components, some of which have recently been forbidden in Europe. Gun propellant residues, mainly nitroglycerin and 2,4-dinitrotoluene, are routinely detected at several firing positions of small, medium and large calibre ammunition.

Metals

Unlike energetic materials, metals are not destroyed during the detonation process. During the detonation, each component of the fusing system and the projectile are disintegrated into fragments of various sizes and dispersed in the environment. Usually, the higher the order of detonation, the smaller the

fragments. Small fragments have a high surface area and are much more prone to be transported away from the impact area through corrosion and dissolution or dispersion in water, or by wind erosion. Consequently, small fragments are those that have the potential to cause the greatest effect on the environment.

Impacted Sites

The most contaminated ranges are usually the smallest sites (demolition, small arms, grenade and anti-tank ranges, and firing positions), on which an accumulation of contaminants can occur. However, artillery impact areas also represent a significant challenge from the perspective of contamination, characterization and remediation. Demolition ranges, on which obsolete ammunition is destroyed by open burning or open detonation and where various demolition activities are practiced, are usually highly contaminated with explosive and propellant residues along with heavy metals. The small arms ranges contain high concentrations of lead, antimony, copper and zinc in the bullet stop berms, and of propellant residues at the firing positions. The grenade ranges are typically characterized by a mixed contamination of explosive residues, copper and zinc. HMX accumulates around targets in the impact area of anti-tank ranges, while propellant residues are preferentially located at firing positions. References (69–87) report the proportion of gun propellant that does not burn completely in the guns during the live firing of specific military ammunitions.

Environmental Fate

A thorough knowledge of the bioavailability, degradation pathways, toxicity and transport properties of munitions-related residues and of their metabolites is crucial to understand their environmental fate and to design appropriate remediation strategies.

Energetic Materials

The environmental fate of energetic materials is mainly related to their water solubility, their adsorption to soil particles and their biotic and abiotic transformations. For instance, TNT is more soluble and dissolves more rapidly in water than RDX or HMX (HMX being the least soluble) (92). In addition, TNT tends to degrade by photolysis, while RDX and HMX do not. The metabolites of TNT all have various solubilities and toxicities. For example, the aminodinitrotoluenes that result from the photolysis or biodegradation of TNT are much more soluble than the parent compound, but they can covalently bind to humic acid. Therefore, these metabolites are stabilized by the formation of an amide with the organic content of the soil. Moreover, in soils that contain clays, the sorption mechanisms are stronger with TNT and its metabolites than for RDX and HMX, which adsorb very poorly to clay minerals. Therefore the relative rates of soil leaching of these three explosives can be explained in terms of the relative water solubilities and adsorption strengths: TNT and its metabolites are more

soluble than RDX, but their migration is inhibited by strong bonding interactions with soil constituents. Therefore, RDX leaches out faster than TNT, which in turn leaches out faster than HMX. However, HMX has a tendency to remain at the surface of the soils, because it is almost insoluble in water.

Interactions with the soil are also important factors to consider when characterizing munitions-related residues in terms of bioavailability and extractability. TNT is particularly difficult to characterize because it is easily reduced to amino degradation products, namely 2- and 4-amino-dinitrotoluene (ADNT), 2,4- and 2,6-diamino-nitrotoluene (DANT), and, under anaerobic conditions, 2,4,6-triaminotoluene (2,4,6-TAT).

The characterization of the degradation products of energetic materials is important in establishing their overall toxicity, remediation, transport, and extractability. The adsorption and desorption characteristics of TNT and its metabolites are important physical factors to consider when assessing the availability of the compounds to microbial degradation and physical analysis.

Metals

The fate and transport of heavy metals in the environment depends strongly on their solubility in water and their bioavailability, i.e. their capacity to bind to the soil constituents. A compound with a high solubility and a low binding capacity has a higher mobility and presents a larger potential for leaching in groundwater and/or travel far away from the range. However, a compound having a low solubility will most probably stay on the surface of the soil, and a compound with strong binding affinities will most probably stay either on the surface or in the subsurface, where a specific bonding agent is encountered.

The water solubility of heavy metals in their elemental state is generally low. However, heavy metals do not generally remain in their elemental form when they are exposed to weathering and water. They are easily oxidized in their ionic form and will form various oxides and salts with soil constituents, each having a different solubility and bioavailability.

As a general rule, nitrates, chlorides, bromides and acetates are readily soluble in water, and sulphides are considered to be insoluble. However, the solubility of hydroxides, sulphates, phosphates, and carbonates will vary depending on the heavy metal component, and on the pH of the water. The lowest solubilities are generally observed in neutral pH water (6.5 to 7.5). Acidic water ($\text{pH} < 6.5$) tends to increase the solubility of most metals salts, while basic water ($\text{pH} > 7.5$) will either induce the precipitation and immobilisation of an insoluble heavy metal compound, or increase its solubility, depending on the heavy metal. Thus, extreme caution must be exercised when trying to decrease the leaching of soils containing multiple heavy metals by controlling the pH of the soil, because the solubility of some heavy metal compounds may increase when exposed to basic pH.

Key parameters governing the bioavailability of a given heavy metal compound are (1) the composition (organic matter, metallic constituents) and pH of the soil, (2) the particle size distribution, and (3) the contact time between water and the heavy metal compound. These parameters govern in turn measurable

macroscopic parameters, such as the type of soil (sand, silt, clay, etc.), the cation exchange capacity (CEC), and the reduction-oxidation (redox) potential.

The binding capacity tends to increase with the decrease in size of soil particles. For example, absorption in clay is much higher than in sand because the groundwater movement in clay is slower, and also because of the high surface area of soil particles to which heavy metal compounds can bind. In consequence, sandy soils present the highest leaching potential.

The contact time between water and the heavy metal compounds is controlled by the amount of annual precipitation and intensity of the rainfall. The adsorption of several heavy metal compounds to soil components also tends to increase with the cation exchange capacity. The redox potential will affect the type of heavy metal compound that is stable in a given area. The bioavailability of heavy metals and factors affecting it is a very complex subject, and a thorough review is beyond the scope of this document. Interested readers may consult appropriate references for more information.

The mobility of heavy metals is also affected by external physical factors, such as the topographic slope and the intensity of wind. Particles of heavy metal compounds or dissolved heavy metals can be moved by storm water runoff. The ability of water to transport lead is influenced by two factors: velocity of the water and weight or size of the lead fragment. Water's capacity to carry small particles is proportional to the square of the water's velocity (92). Clear water moving at a velocity of 100 feet per minute can carry a lead particle 10,000 times heavier than water, moving the particle at a velocity of 10 feet per minute. Muddy water can carry even larger particles. A shallow groundwater table is indicative of potentially higher risk for mobilized heavy metals to reach the groundwater. The shorter the distance traveled, the greater the risk of migration of heavy metals into the environment.

Characterization Approach

The characterization of munitions-related residues poses a significant challenge because of the local and distributional heterogeneity of the distribution of contaminants, and also because of the large diversity of military activities. The large sizes of RTAs (impact areas can reach 10 to 20 km², and bombing areas are much larger than that) also pose a significant challenge for the characterization. It is indeed not possible to obtain samples that are representative of the mean concentration of a whole area.

The characterization approach developed by DRDC Valcartier is to perform the soil surface study concurrently with a detailed hydrogeological study of the site. This approach is carried out as part of a collaborative effort with the *Institut national de la recherche scientifique - Centre Eau, Terre et Environnement* (INRS-ETE). Soil sampling is performed using a multi-increment composite sampling strategy and a systematic/random sampling design specifically adapted to each range, depending on the type of activity occurring on the site. This approach is illustrated in Figure 1; more details can be found in (66).

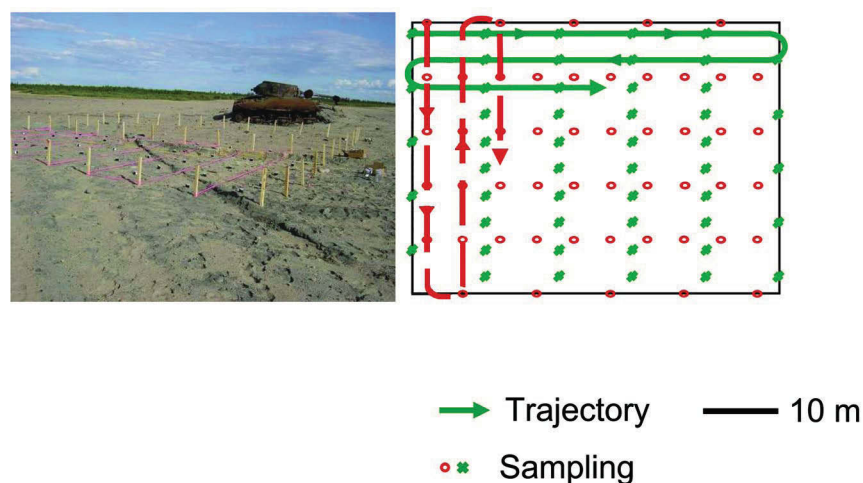


Figure 1. Soil sampling strategy illustrating a systematic sampling design. (see color insert)

Hydrogeology typically provides detailed information on the quality and flow direction of surface water and groundwater, on the water table depth and on the various types of soil on which the ranges are built. The hydrogeological data collected lead to the preparation of several thematic maps (piezometric, surficial geology, etc.), two of which are shown in Figures 2 and 3. The following step is the modeling of groundwater flow. This step is generally performed using a numerical model, such as FEFLOW, which uses input parameters such as piezometry, hydraulic conductivity of the various stratigraphic units, recharge with the HELP model, 3D geological model, etc. This model allows the reproduction of the behaviour of the groundwater at regional and local scales, and the prediction of the transport of contaminants. This is a parameter extremely important to have in order to perform risk analyses of the ecological and human receptors surrounding RTAs. A conceptual model is then built following the 3D geological model and from the knowledge of the environmental fate of energetic materials in the environment. Several monitoring wells are necessary to build a precise conceptual model, to validate this model, and to adequately follow potential contamination in the groundwater. Canada, which has installed several hundreds of monitoring wells in its RTAs, has developed a very proactive military site assessment approach and acts as a world leader in this domain.

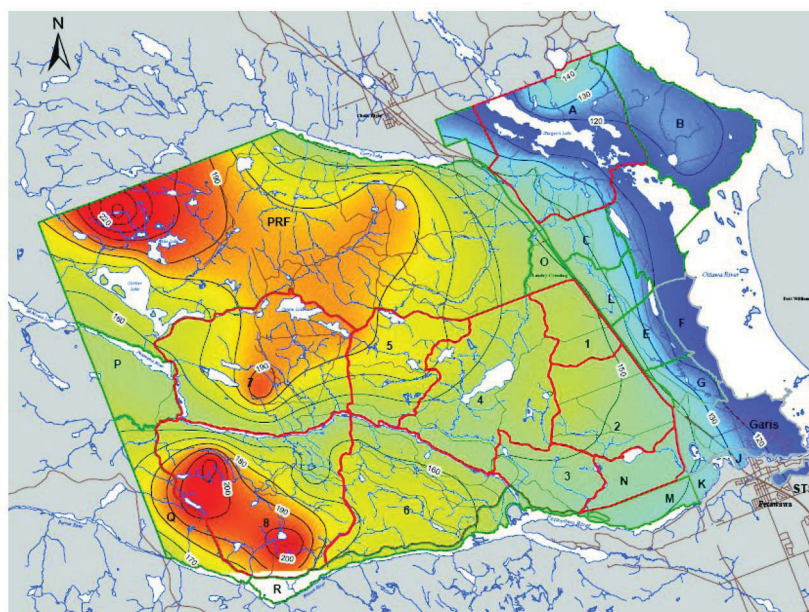


Figure 2. Piezometric map. (see color insert)

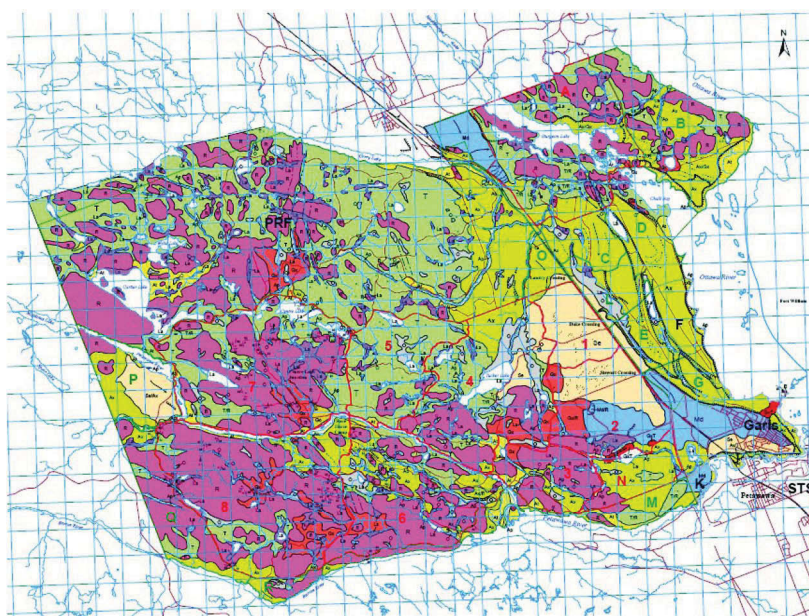


Figure 3. Surficial geology map. (see color insert)

Ecological Risk Assessment

Risk is defined as the probability of an adverse event due to disturbances in the environment:

$$\text{Risk} = \text{Severity of event (Hazard)} \times \text{Exposure}$$

The Ecological Risk Assessment (ERA) of RTAs will attempt to estimate and, where possible, quantify risk posed to the environment and its non-human inhabitants by the presence of munitions-related residues concentrations. It is a complex process involving the participation of a team of professionals with expertise in various disciplines (chemists, munitions specialists, toxicologists, ecologists, hydrogeologists, environmental fate and transport modeling specialists). This ambitious R&D program has been realized by a long-term partnership of DRDC Valcartier, INRS-ETE, and the Biotechnology Research Institute (BRI) of the Canadian National Research Council. The ERA of RTAs involves the following steps:

- Receptor Characterization
- Exposure Assessment
- Hazard Assessment
- Risk Characterization

The Receptor Characterization attempts to identify the ecological (non-human) receptors of concern, the effects against which it is desirable to protect those receptors, and the means or pathways specific to each receptor by which it may come into contact with contaminants (93). This part of the process is carried out by BRI which performs state-of-the-art R&D to evaluate the effect of energetic materials on terrestrial plants, terrestrial animals, soil microorganisms and aquatic species (94–157). BRI also studies the degradation of energetic materials through biotic and abiotic pathways, phytolysis, and chemical degradation. One significant output of their R&D program was the development of the first worldwide ecotoxicological criteria specifically developed for a military scenario (151).

The Exposure Assessment, defined as the evaluation of the potential exposure of the receptors to munitions-related residues, is dealt with using vulnerability maps which reflect the vulnerability of a given aquifer-to- surface contamination and the risks related to soil contamination by residues of energetic materials.

Aquifer vulnerability can be assessed with a method that uses the hydrogeologic properties of the area (infiltration, porosity, permeability, etc.) obtained through the 3D geologic modeling, to estimate the downward advective time (DAT) of travel for infiltration water in the vadose zone from the surface to the water table of the first aquifer.

Vulnerability maps describe the relative ease with which dissolved contaminants reach the upper boundary of an aquifer from land surface by vertical transport/migration, advection, non-retarded, non-reactive transport. It is basically the time it takes a drop of water to travel from the surface of the soil

to the groundwater table. The output is translated into vulnerability maps, an example of which is shown in Figure 4.

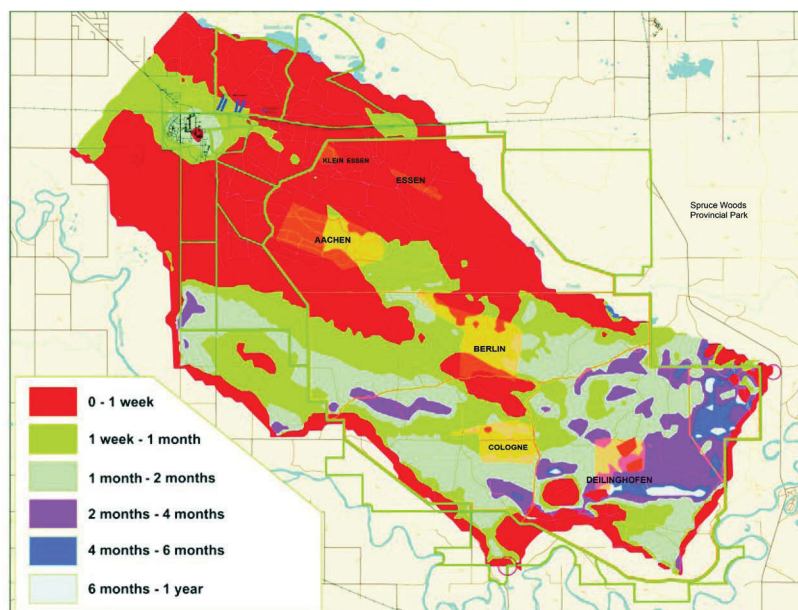


Figure 4. Vulnerability map. (see color insert)

Hazard Assessment is the process of determining the potential for munitions-related residues to cause adverse effects in exposed individuals or populations, and of estimating the relationship between the extent of exposure and the severity of effects. The evaluation of the risk of environmental contamination associated with military activities is performed with an index system specifically developed for military training areas (158) using parameters such as firing frequency, quantity of energetic materials deposited on the training area, solubility and persistence of the contaminants associated with each munitions type, and spatial extent of the contamination. These data are used to generate hazard maps, as shown in Figure 5.

Risk Characterization is the integration of information derived from receptor characterization, exposure assessment and hazard assessment. It gives an estimate of the degree of risk that is present from specified contaminants to the receptors of a given site. Practically, the analysis of the risk of aquifer contamination associated with military training activities is conducted by combining the vulnerability map defined using the DAT approach and the hazard map, taking into account the type of munitions used. The final result is a risk map, as shown in Figure 6.

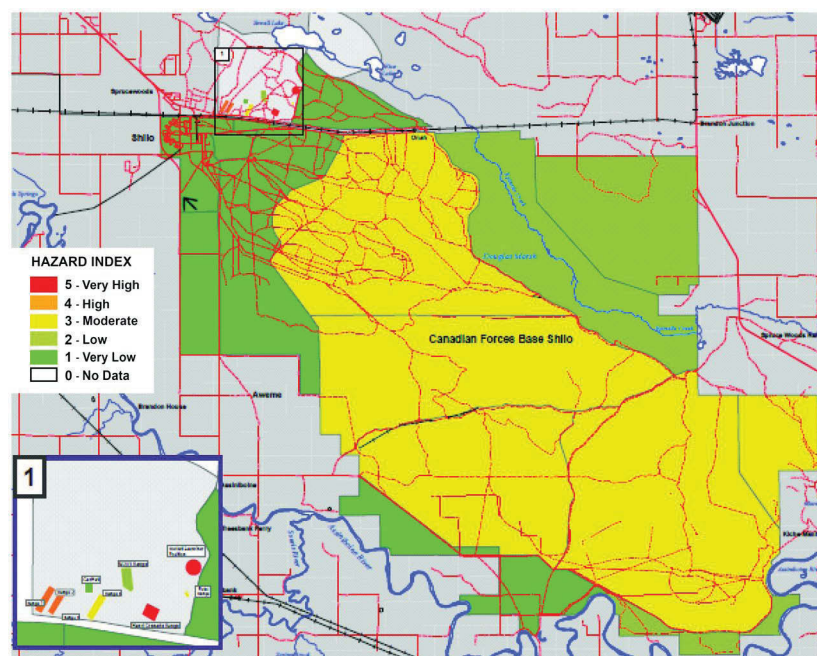


Figure 5. Hazard map. (see color insert)

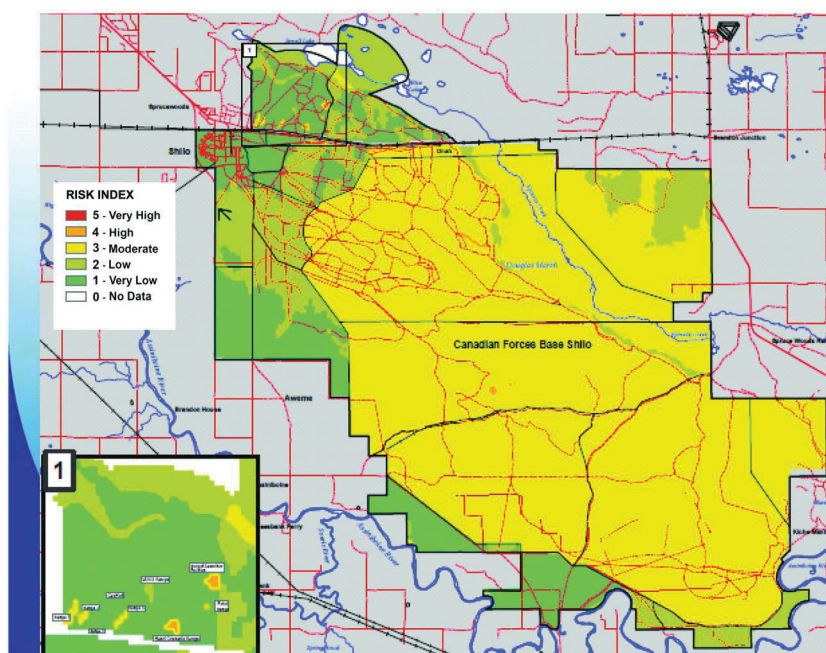


Figure 6. Risk map. (see color insert)

Conclusions

A thorough knowledge of the bioavailability, degradation pathways, toxicity and transport properties of munitions-related residues and of their metabolites is crucial to the understanding of their environmental fate and to design appropriate remediation strategies. Canada is currently developing management tools that will be extremely useful to manage RTAs in a sustainable manner and to reduce the risk associated with military training. The use of vulnerability, hazard and risk maps will enable stakeholders to assess the impacts of military training activities in RTAs. These maps will also help in performing appropriate risk assessments and implementing suitable mitigation and remediation measures from the standpoint of potential for groundwater and surface water contamination. They also represent an invaluable tool to assist in the selection of suitable locations for future training activities and to the establishment of yearly sampling plans for soils, groundwater and surface water. Environmentally-friendly defence activities will help Canada ensure the long-term usage of RTAs that will guarantee military readiness.

Acknowledgments

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